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A PEEM STUDY OF SMALL AGGLOMERATES OF COLLOIDAL IRON OXIDE NANOCRYSTALS

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A common limitation in nanostructure research is often the requirement to perform experiments on ensembles of nanoparticles, therefore averaging over inherent distributions with respect to particle size and shape, chemical composition, crystallinity and defect structure. This limitation can be overcome by studying the properties of a single nanostructure individually, which will allow one to truly correlate scaling laws of material properties with changes in size. Here we report the first experiments to explore the feasibility of spectromicroscopy using a photoemission electron microscope (PEEM) to record the X-ray absorption spectra of *single* nanocrystals. Colloidal iron oxide nanocrystals with an average diameter and standard deviation of 13 nm and 2 nm, respectively, were deposited on graphite (HOPG) forming small islands of agglomerated γ-Fe_2O_3 nanocrystals (4–30 particles) as determined by scanning electron microscopy. Spatially resolved soft X-ray absorption spectra at the Fe $L_{3,2}$ edges of these individual islands were recorded with the PEEM2 instrument of the Advanced Light Source (ALS).

1. Introduction

The development of the electronic structure with the size of nanocrystals and the investigation of size-dependent scaling laws is an active research area of academic and technological relevance.[1–3] In general, experiments are performed on ensembles of nanocrystals, which even in the most favorable cases still exhibit a distribution with respect to particle size and shape, chemical composition, crystallinity or defect structure. In consequence, scaling laws derived from such experiments represent an ensemble average with an inherent uncertainty with respect to intrinsic properties of individual nanocrystals. To overcome these limitations, single particle experiments have been developed and performed in recent years.[4–6] For instance, in optical fluorescence spectroscopy of ensembles of semiconductor nanocrystals one observes typically rather broad fluorescence lines (FWHM ∼0.1–0.2 eV at 10 K). However, experiments on individual nanocrystals yield not only extremely sharp emission lines (FWHM ∼200 μeV at 10 K) but also allow the observation of effects like spectral diffusion and blinking of single nanocrystals, which is impossible in ensemble measurements.[4]

While optical spectroscopy enables the investigation of the size dependence of the optical excitation gap of semiconductor nanocrystals, more detailed information about their electronic structure can be obtained by X-ray core level spectroscopy.[7] X-ray absorption spectroscopy is an established technique which provides elemental, chemical and

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structural information.[8,9] Using polarized X-rays, this technique is sensitive to orientation phenomena like molecular orientation as well as size and orientation of magnetic moments (linear[10] and circular[11] magnetic dichroism). Here we report first experiments to explore the feasibility of spectromicroscopy to record the X-ray absorption spectra of *single* iron oxide nanocrystals with 13 nm average diameter using photoemission electron microscopy (PEEM). To the best of our knowledge no spatially resolved X-ray absorption spectra on a length scale of tenths of nanometers have been reported. However, we note that core level photoelectron studies of surface structures on a submicron length scale have been performed.[12]

2. Experiment and Results

The experiment was carried out with the PEEM2 instrument at the bending magnet beamline 7.3.1.1 of the Advanced Light Source.[13] PEEM is a full field imaging technique which combines two concepts: X-ray absorption spectroscopy and electron microscopy. The X-rays, whose polarization can be changed between linear and right or left circular, are incident on the sample at an angle of 30° from the surface and form a 30 μm spot. The low-energy secondary photoelectrons emitted from the sample are imaged by an electron microscope with magnification onto a phosphor screen that is digitized by a charge-coupled device (CCD) camera. Image contrast can arise from a number of mechanisms including topographical, elemental, chemical, polarization, X-ray magnetic circular (XMDC) and linear dichroism (XMLD). The currently best spatial resolution demonstrated is 20 nm.

Although this is not sufficient to resolve a nanocrystal (typical size 2–15 nm), the spectrum of a single nanocrystal can be obtained if the mean interparticle distance is larger than the spatial resolution. An additional requirement is that the area between the particles contribute as little as possible to the overall signal. The actual coverage, for example whether the nanocrystals are agglomerated or not, has to be measured with another technique like transmission (TEM) or scanning electron microscopy (SEM).

For the initial experiments reported here, dilute toluene solutions of iron oxide nanocrystals (γ-Fe_2O_3, maghemite[14]) with a mean diameter of

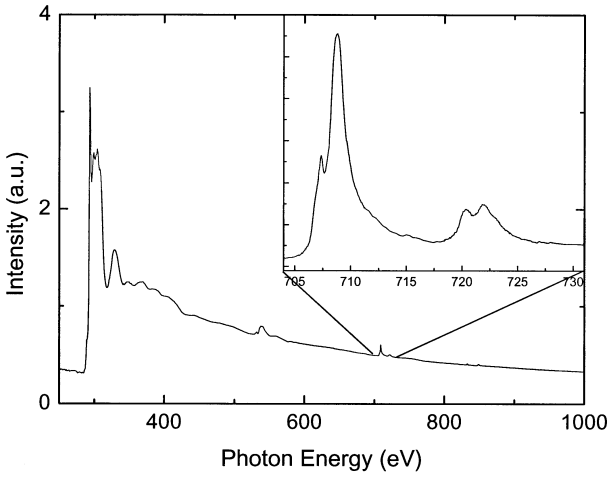
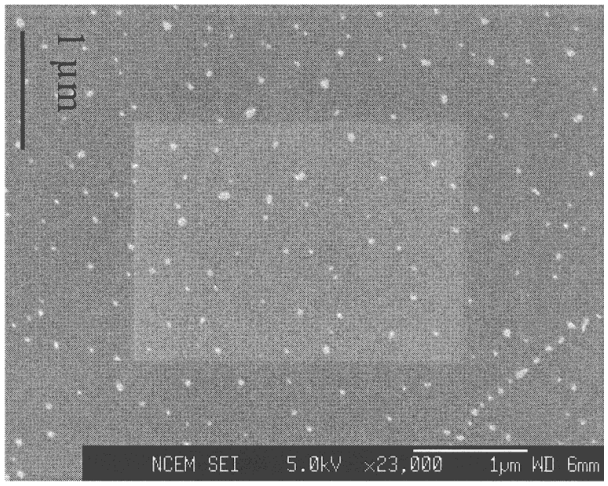


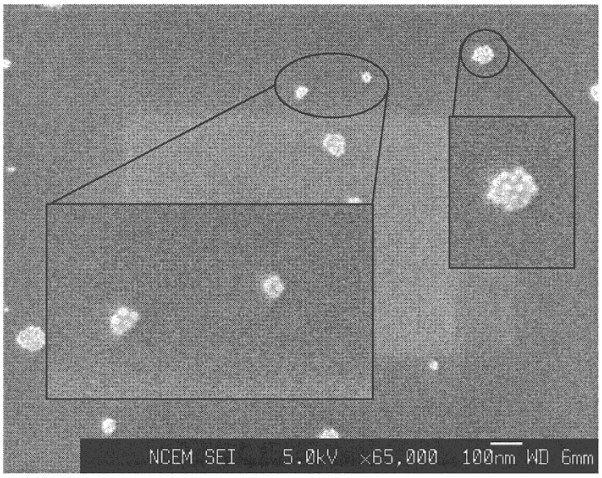
Fig. 1. X-ray absorption spectrum of an ensemble of iron oxide nanocrystals spin-coated on graphite. The inset shows enlarged the iron $L_{3,2}$ edge region (the acquisition time of this not spatially resolved spectrum was 15 min).

(13 ± 2) nm were spin-coated onto freshly cleaved graphite (HOPG). Total electron yield X-ray absorption spectra with high energy resolution of this sample were measured at the wiggler beamline 10-1 at the Stanford Synchrotron Radiation Laboratory using linearly polarized light. These measurements were not spatially resolved and depict the average spectrum of the nanocrystal ensemble. The depth sensitivity is determined by the escape depth of the secondary electrons, which for iron oxide is about 5 nm.[15] Hence the majority of the nanocrystal contributes to the signal and the spectra do not only reflect contributions from the particle surface. The spectrum (see Fig. 1) is dominated by the signal from the graphite substrate with the carbon K-edge around 300 eV and a monotonic decay towards higher photon energies. In comparison the signal from the nanocrystals (around 700 eV) is very small. The inset shows enlarged the iron $L_{3,2}$ edge region with the characteristic multiplet structure of iron oxide.[16,17] In accordance with X-ray diffraction patterns of this sample, the absence of absorption features by Fe^{2+} ions gives evidence that the nanocrystals consist mostly of γ-Fe_2O_3 (only Fe^{3+}) and not Fe_3O_4 (Fe^{3+} and Fe^{2+}).

The SEM image [see Fig. 2(a)] of the investigated sample shows randomly distributed bright spots and, occasionally, spots arranged in lines. The latter are formed by nanocrystals aligning themselves at



(a)



(b)

Fig. 2. Scanning electron microscope image of iron oxide nanocrystals on graphite. The image shows randomly distributed spots and spots arranged in lines (a). The spots consist of agglomeration of 4–30 nanocrystals (b) (the exposure time for each image was 30 s).

steps on the graphite surface. High-resolution SEM imaging [Fig. 2(b)] reveals that all bright spots correspond to agglomerates of 4–30 nanocrystals formed during the deposition process. The average distance between the bright spots is around 250 nm and is therefore sufficiently bigger than the typical spatial resolution of PEEM allowing X-ray absorption spectroscopy of individual groups of nanocrystals.

In order to detect the small X-ray absorption signal from the nanocrystals with PEEM2, the setup was optimized for high flux rather than for high

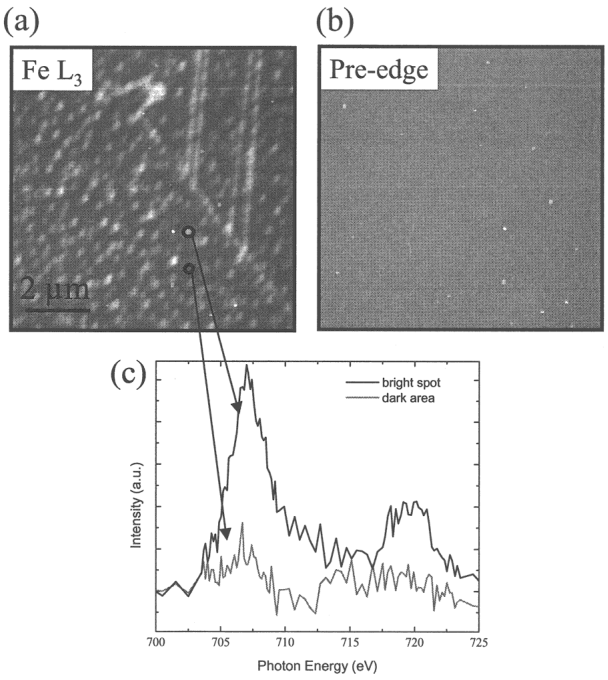


Fig. 3. The PEEM image recorded at the iron L_3 resonant absorption edge [Fig. 3(a)] shows a similar arrangement of bright spot as the SEM image [Fig. 2(b)], whereas these spots are vanished at a pre-edge energy [Fig. 3(b)]. The X-ray absorption spectra recorded from one bright spot and from a dark area are shown in Fig. 3(c). The multiplet structure associated with iron oxide is hardly resolved due to the inherent moderate energy resolution of the beamline, which was further reduced in order to increase the incident photon flux.

spatial or energy resolution, thereby also scarifying the degree of polarization of the X-rays. The energy resolution was approximately $E/\Delta E = 800$ at a photon flux of about 10^{12} photon/s in a 30 μm spot. Tuning the photon energy to the Fe L_3 absorption edge at 707 eV [see Fig. 3(a)], we obtain at the same sample as imaged by SEM in Fig. 2(a) but on a different spot a similar pattern of bright spots and spots arranged into micron-length lines (acquisition time 30 s). However, at a photon energy of 700 eV, i.e. below the Fe L_3 absorption edge, the contrast vanishes [Fig. 3(b)], giving confidence that the iron oxide nanocrystals are the origin of the bright spots. Note that the PEEM image does not depict the real shape of the agglomeration of nanocrystals. First, they appear larger in the PEEM image in Fig. 3(a) compared to the SEM image in Fig. 2(a) since the spatial resolution was only about 150 nm. Second, the elongation of the spots is due to astigmatism of

the first lens that could not be completely corrected for.

Local absorption spectra can be obtained by taking images at each point of a photon energy scan and subsequently calculating the intensity variation for an area as a function of the energy. The exposure time for one image at each X-ray energy point was 7 s, resulting in a total exposure time for one scan of about 20 min. A drift of the images of about 10 pixels (corresponding to 200 nm) was observed, which is due to charging of the sample, and was corrected in order to calculate the spectra. Though it was not possible to record the spectra of a single nanocrystal, since all nanocrystals assembled into small agglomerates upon deposition, we were successful in measuring the X-ray absorption spectra of ensembles of 4–30 iron oxide nanocrystals. The spectrum recorded from one bright spot [see Fig. 3(c)] shows the typical $L_{3,2}$ features of iron oxide, whereas they are absent in the spectrum recorded within a dark area. This clearly demonstrates that the spots in the PEEM image arise from the iron oxide nanocrystals. Note that the multiplet structure associated with iron oxide is hardly resolved due to the inherent moderate energy resolution of the beamline, which was further reduced in order to increase the incident photon flux.

An important finding of our study is that the iron oxide nanocrystals appear to be stable enough to enable X-ray spectromicroscopy measurements and that PEEM can have the necessary sensitivity. In order to achieve single nanocrystal sensitivity we will further optimize the substrate choice as well as the sample preparation techniques to improve the signal-to-noise ratio of the PEEM images. Once the feasibility of PEEM for the spectroscopy of single nanocrystals has been demonstrated, this method can be employed to investigate the properties of individual nanocrystals as a function of size, shape and defect structure. In addition, the unique sensitivity of polarization-dependent X-ray spectromicroscopy to magnetic properties[18] will make PEEM an important tool in the study of magnetic properties of single nanocrystals.

Acknowledgments

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References

1. C. B. Murray, C. R. Kagan and M. G. Bawendi, *Annu. Rev. Mat. Sci.* **30**, 545 (2000).
2. J. Heath, *Acc. Chem. Res.* **32**, Nanoscale Materials Special Issue, 387 (1999).
3. "National Nanotechnology Initiative: Leading to the Next Industrial Revolution," National Science and Technology Council, 2000 (see http://www.nano.gov/).
4. S. Empedocles and M. Bawendi, *Acc. Chem. Res.* **32**, 389 (1999).
5. D. L. Klein, R. Roth, A. L. Lim, A. P. Alivisatos and P. L. McEuen, *Nature* **389**(6652), 699 (1997).
6. H. J. Dai, E. W. Wong and C. M. Lieber, *Science* **272**(5261), 523 (1996).
7. J. Lüning, J. Rockenberger, S. Eisebitt, J. E. Rubensson, A. Karl, A. Kornowski, H. Weller and W. Eberhardt, *Solid State Commun.* **112**(1), 5 (1999).
8. *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XNAES*, eds. D. C. Koninsberger and R. Prins (Wiley, New York, 1988).
9. J. Stöhr, *NEXAFS Spectroscopy*, Springer Series in Surface Science, Vol. 25 (Springer, New York, 1992).
10. B. T. Thole, G. van der Laan and G. A. Sawatzky, *Phys. Rev. Lett.* **55**, 2086 (1985).
11. G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm and G. Materlik, *Phys. Rev. Lett.* **58**, 737 (1987).
12. S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmid and K. C. Prince, *Phys. Rev.* **B63**, 125335 (2001).
13. S. Anders *et al.*, *Rev. Sci. Instrum.* **70**, 3973 (1999).
14. J. Rockenberger, E. C. Scher and A. P. Alivisatos, *J. Am. Chem. Soc.* **121**(49), 11595 (1999).
15. S. Gota, M. Gautier-Soyer and M. Sacchi, *Phys. Rev.* **B62**, 4187 (2000).
16. F. M. F. de Groot, *J. Electron Spectrosc. Relat. Phenom.* **67**, 529 (1994).
17. J. P. Crocombette, M. Pollak, F. Jollet, N. Thromat and M. Gautier-Soyer, *Phys. Rev.* **B52**(5), 3143 (1995).
18. J. Stöhr, H. A. Padmore, S. Anders, T. Stammler and M. R. Scheinfein. *Surf. Rev. Lett.* **5**, 1297 (1998).